Response surface methodology as an efficient tool for optimizing carbon adsorbents for CO₂ capture

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Abstract

Phenol-formaldehyde resins and a low-cost biomass residue, olive stones (OS), were used to prepare five activated carbons for CO₂ separation at atmospheric pressure, i.e., in post-combustion processes or from biogas and bio-hydrogen streams. Two phenol-formaldehyde resins were synthesized: Resol, obtained by using alkaline environment, and Novolac, synthesized in the presence of an acid catalyst. Carbon precursors were prepared by mixing both resins with KCl or by mixing the Novolac resin with OS. The precursors were carbonized under an inert atmosphere of N₂ at different temperatures. The last stage in the synthesis of the adsorbents involved physical activation with carbon dioxide, which was carried out at different temperatures and burn-off degrees. Response surface methodology (RSM) is proposed as a tool for rapidly optimizing the activation parameters in order to obtain the highest possible CO₂ capture capacity of activated carbons. The optimum values of activation temperature and burn-off degree that maximize CO₂ uptake by the activated carbons at 35 °C and atmospheric pressure were obtained within the experimental region. A value of CO₂ adsorption capacity of 9.3 wt.% was achieved. Activated carbons derived from Novolac phenol-formaldehyde

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resin type and from OS showed great potential as adsorbents for CO₂ capture at atmospheric pressure.

Keywords: Phenol-formaldehyde resin; Activation temperature; Burn-off degree; Activated carbon; CO₂ capture; Response surface methodology

1. Introduction

It is widely accepted that climate change is a global phenomenon influenced by greenhouse gas emissions to the atmosphere, CO₂ being the main greenhouse gas contributing to global warming. The main source of CO₂ emissions is the production of energy from fossil fuels. Although some measures are already being implemented, such as increasing the use of renewables and improving the efficiency of energy conversion processes, in the short-to-medium term carbon capture and storage (CCS) will be necessary in order to reduce CO₂ emissions to the atmosphere. CO₂ capture is the most costly component of the CCS process [1]. This has led to intensive research aimed at the production of CO₂ capture materials which can achieve significant levels of CO₂ uptake.

Adsorption is considered one of the most promising technologies for CO₂ capture and different types of adsorbents, such as zeolites and activated carbons, have been used for this purpose [2-4]. Zeolites are the most extensively studied adsorbents of CO₂, due to their high selectivity towards CO₂. However, activated carbons have a high adsorption capacity at ambient pressures and present important advantages over zeolites, such as their hydrophobicity, their significant lower cost and the lower amount of energy needed to regenerate them. Adsorption with activated carbons at atmospheric pressure is a useful technology for postcombustion CO₂ capture, as well as for the

separation of CO₂ from CH₄/CO₂ or H₂/CO₂ mixtures to obtain a stream of high pure methane or bio-hydrogen, respectively.

The process most frequently used to capture CO₂ at industrial scale is chemical absorption with amines. Nevertheless, this technology has certain drawbacks, such as the high energy requirement for sorbent regeneration, amine losses due to evaporation, corrosion problems or the thermal and chemical degradation of the amines in the presence of oxygen. On the other hand, to separate CO₂ from biogas streams, many technologies are used, such as water washing, amine scrubbing or vacuum pressure-swing adsorption (VPSA). Amine scrubbing is the most economical upgrading process, but only for high flowrates. VPSA seems to be a suitable process for locations with small and medium flowrates and with mild temperatures [5].

The adsorption capacity of an activated carbon is mainly dependent on its pore structure but it is also strongly influenced by its surface chemistry. These materials can be obtained from almost any carbonaceous product by a process of carbonization followed by an activation step. However, the use of naturally occurring precursors to produce activated carbons limits the purity, strength and physical form of the end-product materials. This drawback can be overcome by using polymeric precursors, where the reproducibility and purity of the precursor is within the control of the manufacturer, and the physical forms and structures can be tailored by means of the polymer production process [6]. Phenolic resins constitute a family of low-cost polymers, one of the most common being those produced from phenol and formaldehyde [7]. Phenolic resin-based activated carbons offer further advantages in that they can be produced in a wide variety of physical forms (e.g., granular or extruded, as fibres or as monolithic structures), they allow a close control of porosity, and they

have a very low level of impurities and a good physical strength [7-9]. Furthermore, biomass residues, such as olive stones, are a low-cost and relatively abundant by-product that can be used as a feedstock for the production of microporous activated carbons [10-11].

Response surface methodology (RSM) is a multivariate statistical technique used to optimize processes, i.e., to discover the conditions in which to apply a procedure in order to obtain the best possible response in the experimental region studied. This methodology involves the design of experiments and multiple regression analysis as tools to assess the effects of two or more independent variables on dependent variables [12]. One additional advantage is the possibility of evaluating the interaction effect between the independent variables on the response. This technique is based on the fit of a polynomial equation to the experimental data to describe the behaviour of a set of data. In this way, a mathematical model which describes the studied process is generated. The objective is to simultaneously optimize the levels of the studied variables to attain the best possible performance of the process [13]. Recently, a number of works have been published on the application of RSM to matters related with CO₂ adsorption. For example, Serna-Guerrero et al. [14] studied the optimum regeneration conditions (the temperature, pressure and flow rate of purge gas) of an amine-bearing adsorbent for CO₂ removal, whereas Mulgundmath and Tezel [15] investigated the optimization of carbon dioxide recovery from a flue gas in a TPSA system in relation to the purge/feed flow ratio, purge time, purge gas temperature and adsorption pressure. García et al. [16] studied the combined effect of CO₂ partial pressure and temperature on CO₂ capture capacity and breakthrough time of a commercial activated carbon.

In the present work, phenol-formaldehyde resins and olive stones were employed as precursor materials for the preparation of microporous activated carbons for use in the separation of CO₂. They could then be used to capture CO₂ in post-combustion processes or from biogas and bio-hydrogen streams. The CO₂ capture capacity of the different activated carbons was optimized in relation to temperature and burn-off degree during the activation stage by means of response surface methodology. A rapid assessment method for studying the activation conditions was proposed using a thermogravimetric analyzer. Martín et al. [6] found that intensification of the activation process did not enhance the capture capacity of some activated carbons, whereas for others it did. This shows that every activated material requires specific activation conditions. On the other hand, an increase in the burn-off degree could be justified, economically speaking, if a significant increase in the working capacity of the adsorbent were attained, since, as the burn-off increases, the pore volume gradually develops at the expense of a reduction in the final carbon yield. The objective of this study was to determine the optimum values of activation temperature and burn-off degree for each activated carbon, so as to maximize the CO₂ capture capacity within a given experimental region.

2. Materials and methods

2.1. Synthesis of materials

Phenol-formaldehyde resins and a low-cost biomass residue from the Spanish food industry, olive stones (OS), were used as starting materials. Two types of phenol-formaldehyde resins were synthesized. The first one was obtained by basic catalysis using sodium hydroxide (NaOH) and is commonly referred to as *Resol*. In this case a

2.5:1 formaldehyde-to-phenol ratio was used to obtain the Re resin sample. The second type of resin was synthesized by acid catalysis with hydrochloric acid (HCl) and is known as *Novolac*. In this case two formaldehyde-to-phenol mole ratios were used, 1:1 and 1:1.22, to yield the No1 and No2 resin samples respectively. Phenol (99.4%, BDH Prolabo) and formaldehyde (37 wt.% in H₂O, BDH Prolabo) were employed to synthesize the resins. During the synthesis, the phenol-formaldehyde solution was mixed with the catalyst (acid or basic) in a flask equipped with a reflux condenser, stirred and heated up to the desired temperature (95-100 °C). Once the synthesis had ended, the resins were cured, first in a rotary evaporator at 40-70 °C under vacuum (absolute pressure 48-100 mbar) and then in a forced-air convection oven at 60-100 °C. Finally, the cured resins and the olive stones were ground and sieved to obtain a particle size fraction of 1.0-3.35 mm.

Carbon precursors were then prepared by incorporating potassium chloride (KCl) to the Re and No1 cured resins, which were impregnated with KCl at ambient temperature (ReKCl_a and No1KCl_a precursors) or boiled with a saturated KCl solution (ReKCl_b and No1KCl_b precursors). However, the No2 cured resin was used as additive to the olive stones in a 80:20 wt. proportion of OS:resin. This blend was then mixed with hexamethylenetetramine (28.6%) and heated at 170 °C for 30 min (No2OS precursor). The precursors were then carbonized in a horizontal furnace under a nitrogen flow rate of 50 mL min⁻¹. The ReKCl_a and No1KCl_a precursors, prepared at ambient temperature, were carbonized at 600 °C, which yielded the ReKCl_a-600 and No1KCl_a-600 carbonized samples. The ReKCl_b and No1KCl_b precursors, prepared at boiling temperature, were carbonized at 1000 °C, to give the ReKCl_b-1000 and

No1KClb-1000 carbonized samples. Finally, the No2OS precursor was carbonized at 1000 °C, to give the No2OS-1000 carbonized sample.

2.2. Study of physical activation with CO₂ using the response surface methodology

The carbonized materials were physically activated with CO₂ in a thermobalance in a 10 mL min⁻¹ stream of CO₂ at different temperatures. The duration of the activation process was dependent on the degree of burn-off. The response surface methodology (RSM) was used to evaluate the effect of temperature and burn-off degree during the activation stage on the CO₂ capture capacity of the activated carbons. The objective of this study was to determine the optimum values of activation temperature and burn-off degree that would maximize the CO₂ capture capacity of each activated carbon at 35 °C and atmospheric pressure.

In this work, the independent variables were the activation temperature (T) and the burn-off degree attained after the activation process (B), while the dependent variable was the CO₂ capture capacity. The levels of the independent variables are the different values at which the experiments must be carried out. Both independent variables were investigated at three levels, which varied depending on the carbonized material studied.

Before applying the RSM methodology, an experimental design was chosen, which defined what experiments had to be carried out in the experimental region under study as a set of different combinations of the levels of the independent variables. In this work a three-level full factorial design was chosen. This involved 13 experiments, which are shown in Table 1, including nine factorial points and four additional replicates at the centre of the design by means of which it was possible to estimate the

experimental error associated with the repetitions. All the experiments were executed in a random order.

In order to choose the activation temperature range for each carbonized material, a non-isothermal profile under CO₂ (flow rate, 50 mL min⁻¹) up to 1000 °C (heating rate, 15 °C min⁻¹) was obtained for each carbonized sample using a Setaram TGA 92 thermogravimetric analyzer. From these profiles, the temperature of commencement of mass loss was assumed as the minimum activation temperature for each sample. Afterwards, isothermal profiles under CO₂ (flow rate, 10 mL min⁻¹) at the selected activation temperatures were performed in order to calculate the time necessary to obtain the different selected burn-off degrees.

The levels of the independent variables, i.e. activation temperature and burn-off degree, were coded so that variables with different units or of different orders of magnitude could be compared. The responses would then be evenly affected, making the units of the parameters irrelevant. Codification of the levels of the variables consisted in transforming each studied real value into coordinates inside a scale with dimensionless values, which are proportional to their location in the experimental space. In Table 1 the coded values of the independent variables for all of the activated carbons are shown in parentheses. The experimental values obtained for the response variable, CO₂ capture capacity, for all of the activated carbons are presented in Table 2.

The mathematical-statistical treatment of the experimental data consisted in fitting a polynomial function to the set of data. In this work, with two independent variables, x_1 and x_2 , the following second-order polynomial equation was used:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \varepsilon \quad (1)$$

where β_0 is the constant term, β_1 and β_2 represent the coefficients of the linear parameters, β_{12} represents the coefficient of the interaction parameter, β_{11} and β_{22} represent the coefficients of the quadratic parameters and ε is the residual associated with the experiments. Multiple regression analysis was used to fit Eq. (1) to the experimental data by means of the least-squares method, which makes it possible to determine the β coefficients that generate the lowest possible residual. The equation obtained describes the behaviour of the response in the experimental region as a function of the independent variables.

Evaluation of the fitness of the models was carried out by applying an analysis of variance (ANOVA) and a lack of fit test. A model will fit the experimental data well if it presents a significant regression and a non-significant lack of fit. To establish whether a parameter is significant, a p -value test with a 95% level of confidence was applied to the experimental results. The coefficient of determination adjusted by the number of variables ($\text{Adj-}R^2$) and the absolute average deviation (AAD) were calculated in order to check the accuracy of the model. $\text{Adj-}R^2$ must be close to 1.0 and the AAD between the predicted and observed data must be as small as possible. $\text{Adj-}R^2$ represents the proportion of variability of the data that is accounted for by the model. The AAD is a direct parameter that describes the deviations between the experimental and calculated values and it is calculated by means of the following equation [17]:

$$\text{AAD (\%)} = 100 [\sum_{i=1}^n (|y_{i,\text{exp}} - y_{i,\text{cal}}|/y_{i,\text{exp}})]/n \quad (2)$$

where $y_{i,\text{exp}}$ and $y_{i,\text{cal}}$ are the experimental and calculated responses, respectively, and n is the number of experiments. The statistical analyses were carried out by SPSS Statistics 17.0 software.

The model obtained can be three-dimensionally represented as a surface (response surface plot) and the best operational conditions inside the studied experimental region can be found by visual inspection. A two-dimensional display of the surface plot generates the contour plot, where the lines of constant response are drawn on the plane of the independent variables. Response surface and contour plots were generated using the software SigmaPlot 8.0. In this way, it was possible to obtain the optimum values for each studied independent variable that would optimize the response in the experimental region studied.

2.4. CO₂ capture capacity

The CO₂ capture capacity of the adsorbents at 35 °C and atmospheric pressure was assessed in a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer. Prior to the adsorption measurements, the samples were dried at 100 °C under an inert atmosphere (Ar, 50 mL min⁻¹). Afterwards, a CO₂ adsorption test was conducted under a CO₂ flow rate of 100 mL min⁻¹ at 35 °C up to constant weight. The maximum CO₂ uptake at atmospheric pressure and 35 °C was evaluated from the increase in mass experienced by the sample and it was expressed in terms of mass of CO₂ per mass of dry adsorbent.

3. Results and discussion

3.1. Validation of the methodology of activation in a thermogravimetric analyzer

In order to evaluate the possibility of carrying out the activation process in a thermobalance as a rapid method for the evaluation of the activation parameters, experiments of activation with CO₂ were performed in a vertical furnace and in a thermogravimetric analyzer. The No2OS-1000 carbonized material was used for this

purpose. Firstly, a non-isothermal profile under CO₂ (flow rate, 50 mL min⁻¹; heating rate, 15 °C min⁻¹) up to 1000 °C was obtained for the carbonized material using a Setaram TGA 92 thermogravimetric analyzer. Fig. 1a shows the mass loss of the sample as a function of temperature. From this profile, an activation temperature of 950 °C was selected for the comparison of the results obtained from the thermogravimetric analyzer and furnace.

An isothermal profile under CO₂ at 950 °C was then carried out. Firstly, the carbonized sample was maintained at room temperature under an inert atmosphere (Ar, 50 mL min⁻¹) for 10 min and then was heated up to 950 °C (heating rate, 50 °C min⁻¹), this temperature being maintained for 10 min. Then, the atmosphere was changed to CO₂ (flow rate, 10 mL min⁻¹) and the temperature was maintained at 950 °C for 10 h. Finally, the sample was cooled down to room temperature under inert atmosphere (Ar, 50 mL min⁻¹; cooling rate, 50 °C min⁻¹). Fig. 1b shows the mass loss of the sample as a function of time. The time needed to obtain the selected burn-off degree was determined from this plot. Thus, carbons with degrees of burn-off of 29 and 38% were obtained after total times of 58 and 64 min (i.e. 20 and 26 min under CO₂ atmosphere), respectively.

Simultaneous activation experiments with CO₂ were carried out in a vertical furnace (500 mg of sample approximately) in a 10 mL min⁻¹ stream of CO₂ up to 950 °C. The duration of the activation processes were 1.1 and 1.3 h and carbons with burn-off degrees of 28 and 40%, respectively, were obtained.

The CO₂ capture capacity of the activated carbons, obtained in the thermobalance and vertical furnace, was assessed in a Mettler Toledo TGA/DSC 1 thermogravimetric analyzer, as explained above. Fig. 1c shows the CO₂ capture capacity

at 35 °C and atmospheric pressure with time for the activated carbons obtained in the thermobalance and in vertical furnace. As can be seen, the samples obtained in both experimental devices presented similar behaviours under these conditions, i.e., the CO₂ capture capacity increased with the increase in burn-off degree. In addition, the differences in capture capacity between carbons were very small. It can be seen that the CO₂ capture capacity of the samples obtained in the thermobalance was only slightly higher (around 0.2%) than that of the samples activated in the furnace.

The structure of the activated carbons obtained in the furnace and thermobalance is undoubtedly different. However, from these results, it can be concluded that the CO₂ activation in a thermogravimetric analyzer may be used as a reliable tool to rapidly assess the effect of the activation parameters on the CO₂ capture capacity.

Therefore, to study the CO₂ capture capacity as a function of the activation characteristics using response surface methodology, the thermobalance was used in order to reduce the experimental time.

3.3. Optimization of the activation parameters by response surface methodology

A systematic study using RSM has been carried out to examine the combined effect of activation temperature and burn-off on CO₂ capture capacity. Tables 3 and 4 show the results of fitting Eq. (1) to the experimental data by multiple regression analysis, and those obtained from evaluating the fitness of the model by means of ANOVA, together with the Adj- R^2 and AAD values.

The ANOVA tests showed that the models for CO₂ capture capacity were statistically significant at a 95% confidence level (p -value<0.05), whereas their lack-of-

fit was found to be statistically non-significant at a 95% confidence level (p -value >0.05).

Tables 3 and 4 also show which of the terms in the models were statistically significant at a 95% confidence level (p -value <0.05), and those that were not statistically significant (p -value >0.05) were eliminated from the models. The Adj- R^2 and the AAD values were found to be acceptable, between 0.806-0.949 and 1.4-8.1%, respectively.

Once the non-significant terms were eliminated, the coded coefficient values were decoded in order to obtain the polynomial models for the response variables as a function of the true independent variables. The models obtained for all the activated carbons were as follows:

$$\text{CO}_2 \text{ uptake}_{\text{ReKCl a-600}} (\text{wt.}\%) = -56.5446 + 0.1710 T + 0.1863 B - 0.0003 T \cdot B - 0.0001 T^2 \quad (2)$$

$$\text{CO}_2 \text{ uptake}_{\text{ReKCl b-1000}} (\text{wt.}\%) = -97.8905 + 0.2782 T + 0.0367 B - 0.0002 T^2 \quad (3)$$

$$\text{CO}_2 \text{ uptake}_{\text{No1KCl a-600}} (\text{wt.}\%) = -20.4159 + 0.0668 T + 0.2134 B - 0.0002 T \cdot B - 0.00004 T^2 - 0.0016 B^2 \quad (4)$$

$$\text{CO}_2 \text{ uptake}_{\text{No1KCl b-1000}} (\text{wt.}\%) = -17.4048 + 0.0622 T - 0.00004 T^2 \quad (5)$$

$$\text{CO}_2 \text{ uptake}_{\text{No2OS-1000}} (\text{wt.}\%) = -187.2095 + 0.4129 T - 0.0002 T^2 \quad (6)$$

Figs. 2 and 3 present the response surface plots and the contour plots for the CO₂ capture capacity as a function of the independent variables, activation temperature and burn-off, for all the activated carbons. For the ReKCl a-600 material (Fig. 2a), at high temperatures the CO₂ capture capacity decreased as the degree of burn-off increased. However, at lower temperatures this effect was not very noticeable and the burn-off had very little influence on CO₂ uptake. This is shown by the interaction term, $T \cdot B$, in Eq.

(2). In addition, a curvature can be seen in the response surface and the contour plot isolines, indicating that a maximum response is obtained in the temperature range studied. This is also shown by the quadratic term, T^2 , in Eq. (2). Thus, the highest CO₂ capture capacity (3.6 wt.%) was obtained at an activation temperature of 694 °C and a burn-off degree of 10%. Below this temperature, CO₂ capture capacity was hardly affected at all by the burn-off degree, while above this temperature, CO₂ uptake decreased with burn-off. This may indicate that at high temperatures the activation is so severe that the increase in the burn-off value probably causes a reduction in the micropore volume due to the collapse of adjacent pore walls, resulting in a lower CO₂ capture capacity.

For the ReKClb-1000 carbonized material (Fig. 2b), the CO₂ capture capacity increased as the degree of burn-off increased over the entire temperature range studied, since no interaction effect between T and B was detected in the experimental region under study (the T·B interaction term was not statistically significant as shown in Table 3). A curvature was also observed, indicating the achievement of a maximum response. In this case, the highest CO₂ capture capacity (4.4 wt.%) was obtained at an activation temperature of 722 °C and a burn-off of 50%.

For the No1KClc-600 carbonized material (Fig. 3a), a curvature was found in relation to both independent variables studied, as is shown by the quadratic terms, T^2 and B^2 , in Eq. (4). This indicates that a maximum response was achieved within the experimental region considered. The behaviour of this sample was similar to that described for ReKClc-600. For No1KClc-600 material the highest CO₂ capture capacity (9.3 wt.%) was obtained with an activation temperature of 809 °C and a burn-off of 22%.

Finally, for the No1KClb-1000 and the No2OS-1000 carbonized materials (Figs. 3b and 3c) the burn-off degree had no effect on CO₂ uptake, whereas a maximum response was obtained in relation to the temperature. For both materials, the CO₂ uptake values within the experimental region only changed inside a very narrow range and it might cause the non-significant effect of the burn-off degree. For No1KClb-1000 the highest CO₂ capture capacity (7.5 wt.%) was achieved at an activation temperature of 800 °C, whereas for No2OS-1000 the highest CO₂ capture capacity (7.3 wt.%) was obtained at 942 °C, irrespective of the burn-off value.

Therefore, it can be concluded that, in the experimental region studied, the activation parameters do not similarly influence the capture capacity of all the evaluated samples. Furthermore, RSM applied to thermogravimetric data is a useful tool to carry out the optimization of the activation process.

As pointed out above, the highest CO₂ uptake at atmospheric pressure and 35 °C corresponded to the No1KClb-600 activated carbon, which reached 9.3 wt.%. The No1KClb-1000 and No2OS-1000 samples presented relatively high CO₂ uptake values (around 7.5 wt.%). These values are in good agreement with those of commercial activated carbons used for CO₂ adsorption [18]. On the other hand, the lowest values of CO₂ uptake corresponded to the activated samples from the *Resol* basic resin, ReKClb-600 and ReKClb-1000 (3.6 and 4.4 wt.%, respectively).

The results obtained in this work will be used to produce adsorbents at the optimum activation conditions on a larger scale and to evaluate their CO₂ capture performance in mixtures of CO₂/N₂, CO₂/CH₄ and CO₂/H₂. To this end, CO₂ adsorption-desorption cyclic tests will be conducted in a purpose-built lab-scale fixed bed reactor.

4. Conclusions

Carbon adsorbents prepared from phenol-formaldehyde resin type Novolac, and a mixture of this type of resin (20 wt.%) with olive stones (80 wt.%), presented CO₂ adsorption capacity values, at 35 °C and atmospheric pressure, similar to those of commercial activated carbons (7.3-9.3 wt.%). Response surface methodology was successfully used to evaluate the combined effect of activation temperature and burn-off degree on the CO₂ capture capacity of phenol-formaldehyde resin and olive stone-based activated carbons. When interaction between T and B was detected in the experimental region under consideration, at high activation temperatures the CO₂ uptake decreased with the increase in burn-off, while at low temperatures the burn-off had very little influence on CO₂ uptake. In the absence of interaction, the effect of burn-off was low or nil over the temperature range studied. The optimum activation conditions (temperature and burn-off degree) for maximizing CO₂ uptake were determined for all the samples.

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Figure captions

Fig. 1. Validation of the methodology of activation in a thermobalance using the No2OS-1000 carbonized sample: (a) Non-isothermal profile in CO₂; (b) Isothermal profile in CO₂ at 950 °C; (c) CO₂ uptake at 35 °C and atmospheric pressure of activated carbon samples (activation temperature = 950 °C) obtained in a thermobalance and an oven.

Fig. 2. Response surface and contour plots for CO₂ capture capacity as a function of the activation temperature and burn-off corresponding to the *Resol* phenol-formaldehyde resin-based activated carbons: (a) ReKCl_a-600 and (b) ReKCl_b-1000.

Fig. 3. Response surface and contour plots for CO₂ capture capacity as a function of the activation temperature and burn-off corresponding to the *Novolac* phenol-formaldehyde resin-based activated carbons: (a) No1KCl_a-600, (b) No1KCl_b-1000 and (c) No2OS-1000.

Table 1. Levels of the independent variables, i.e. activation temperature (T) and burn-off degree (B), for all the activated carbons using a three-level full factorial design

Run	ReKClA-600 and ReKClB-1000		No1KClA-600 and No1KClB-1000		No2OS-1000	
	T (°C)	B (%)	T (°C)	B (%)	T (°C)	B (%)
1	600 (-1)	10 (-1)	600 (-1)	10 (-1)	900 (-1)	30 (-1)
2	600 (-1)	30 (0)	600 (-1)	30 (0)	900 (-1)	40 (0)
3	600 (-1)	50 (+1)	600 (-1)	50 (+1)	900 (-1)	50 (+1)
4	700 (0)	10 (-1)	800 (0)	10 (-1)	950 (0)	30 (-1)
5	700 (0)	30 (0)	800 (0)	30 (0)	950 (0)	40 (0)
6	700 (0)	50 (+1)	800 (0)	50 (+1)	950 (0)	50 (+1)
7	800 (+1)	10 (-1)	1000 (+1)	10 (-1)	1000 (+1)	30 (-1)
8	800 (+1)	30 (0)	1000 (+1)	30 (0)	1000 (+1)	40 (0)
9	800 (+1)	50 (+1)	1000 (+1)	50 (+1)	1000 (+1)	50 (+1)
10	700 (0)	30 (0)	800 (0)	30 (0)	950 (0)	40 (0)
11	700 (0)	30 (0)	800 (0)	30 (0)	950 (0)	40 (0)
12	700 (0)	30 (0)	800 (0)	30 (0)	950 (0)	40 (0)
13	700 (0)	30 (0)	800 (0)	30 (0)	950 (0)	40 (0)

Table 2. Experimental values of CO₂ capture capacity for all the activated carbons using a three-level full factorial design

Run	CO ₂ capture capacity (%)				
	ReKCl-a-600	ReKCl-b-1000	No1KCl-a-600	No1KCl-b-1000	No2OS-1000
1	2.4	0.8	7.0	6.7	6.8
2	2.7	0.8	7.5	6.4	7.0
3	2.4	0.7	7.3	5.8	7.0
4	3.5	2.5	8.6	7.0	7.1
5	3.1	3.8	9.3	7.7	7.5
6	2.1	5.0	8.1	7.3	7.5
7	2.5	1.1	8.3	6.2	6.5
8	0.4	3.2	7.4	5.7	6.7
9	0.0	3.1	5.8	4.7	6.6
10	3.0	3.7	9.1	7.9	7.2
11	3.3	3.0	9.3	7.3	7.1
12	2.7	3.6	9.5	7.5	7.3
13	2.9	3.2	9.1	7.6	7.5

Table 3. Results of multiple regression analysis and ANOVA used to fit the polynomial model to the CO₂ capture capacity experimental data of the *Resol* phenol-formaldehyde resin-based activated carbons

	Coded coefficient	Sum of squares	DF	<i>p</i> -value
ReKClA-600				
Intersection	2.934	49.945	1	0.000
T	-0.767	3.527	1	0.000
B	-0.650	2.535	1	0.001
TB	-0.625	1.563	1	0.002
T ²	-1.221	4.115	1	0.008
B ²	0.029	0.002	1	0.001
Model		12.353	5	0.890
Residual		0.804	7	
Total		13.157	12	
Lack-of-fit		0.604	3	0.106
Pure error		0.200	4	
<i>R</i> ²	0.939			
Adj- <i>R</i> ²	0.895			
AAD (%)	4.42			
ReKClB-1000				
Intersection	3.579	74.306	1	0.000
T	0.850	4.335	1	0.007
B	0.733	3.227	1	0.014
TB	0.525	1.103	1	0.100
T ²	-1.878	9.737	1	0.001
B ²	-0.128	0.045	1	0.714
Model		20.696	5	0.002
Residual		2.156	7	
Total		22.852	12	
Lack-of-fit		1.684	3	0.083
Pure error		0.472	4	
<i>R</i> ²	0.906			
Adj- <i>R</i> ²	0.838			
AAD (%)	8.12			

Table 4. Results of multiple regression analysis and ANOVA used to fit the polynomial model to the CO₂ capture capacity experimental data of the *Novolac* phenol-formaldehyde resin-based activated carbons

	Coded coefficient	Sum of squares	DF	<i>p</i> -value
No1KCl-a-600				
Intersection	9.183	489.074	1	0.000
T	-0.050	0.015	1	0.643
B	-0.450	1.215	1	0.003
TB	-0.700	1.960	1	0.001
T ²	-1.540	6.547	1	0.000
B ²	-0.640	1.130	1	0.004
Model		14.595	5	0.000
Residual		0.448	7	
Total		15.043	12	
Lack-of-fit		0.336	3	0.107
Pure error		0.112	4	
<i>R</i> ²	0.970			
Adj- <i>R</i> ²	0.949			
AAD (%)	1.95			
No1KCl-b-1000				
Intersection	7.566	331.975	1	0.000
T	-0.383	0.882	1	0.042
B	-0.350	0.735	1	0.057
TB	-0.150	0.090	1	0.453
T ²	-1.429	5.642	1	0.000
B ²	-0.329	0.300	1	0.190
Model		9.816	5	0.002
Residual		0.996	7	
Total		10.812	12	
Lack-of-fit		0.796	3	0.070
Pure error		0.200	4	
<i>R</i> ²	0.908			
Adj- <i>R</i> ²	0.842			
AAD (%)	7.36			
No2OS-1000				
Intersection	7.334	312.009	1	0.000
T	-0.167	0.167	1	0.030
B	0.117	0.082	1	0.098
TB	-0.025	0.003	1	0.748
T ²	-0.521	0.749	1	0.001
B ²	-0.071	0.014	1	0.459
Model		1.233	5	0.003
Residual		0.157	7	
Total		1.391	12	
Lack-of-fit		0.029	3	0.822
Pure error		0.128	4	
<i>R</i> ²	0.887			
Adj- <i>R</i> ²	0.806			
AAD (%)	1.39			

Fig. 1.

(a)

(b)

(c)

Fig. 2.

Fig. 3.